

**PROCESS FOR LOW TEMPERATURE CLEAVAGE OF AN OXIDATION  
MIXTURE COMPRISING HYDROPEROXIDES**

5 [0001] The present application claims the benefit of  
pending U.S. Provisional Patent Application Serial No.  
60/447,845, filed February 14, 2003.

**Field of the Application**

10 [0002] The present application relates to a process for  
cleaving an oxidation product comprising s-butyl benzene  
hydroperoxide and/or cumene hydroperoxide which reduces  
the production of non-recoverable by-products from  
dimethylbenzyl alcohol (DMBA) and ethyl methyl benzyl  
carbinol (EMBA).

15 **Background**

[0003] In general, phenol is manufactured by oxidizing  
cumene to form the hydroperoxide of cumene, followed by  
cleavage of the cumene hydroperoxide with an inorganic  
acid such as sulfuric acid to form a cumene hydroperoxide  
20 cleavage product. Some processes oxidize s-butylbenzene,  
either alone or in combination with cumene, to produce s-  
butylbenzene hydroperoxide.

[0004] A cumene oxidation product generally contains  
dimethylbenzyl alcohol (DMBA). Where the oxidation feed  
25 comprises s-butylbenzene, the oxidation product also  
generally comprises ethyl methyl benzyl carbinol (EMBA).  
It is desirable to maximize conversion of DMBA in the  
oxidation product to  $\alpha$ -methyl styrene (AMS), and to  
maximize conversion of EMBA in the oxidation product to  
30  $\alpha$ -ethyl styrene (AES) and 2-phenyl-2-butene (2P2B)  
because these compounds can be hydrogenated to produce  
cumene and s-butylbenzene for recycle back to the  
oxidation reactors, which increases overall conversion  
efficiency.

35 [0005] Unfortunately, many cleavage reactions are run at  
relatively high reaction temperatures. For example, the  
reaction temperature in typical boiling pot reactions is  
from about 75 °C to about 85 °C. At such high reaction  
temperatures, significant amounts of DMBA, EMBA, product

AMS, product AES, and product 2P2B are converted to "non-recoverable by-products."

[0006] Methods are needed which decrease the loss of DMBA and EMBA to non-recoverable by-products.

5 **Summary**

[0007] The present application provides a process for cleaving one or more hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof. The process  
10 comprises:  
    feeding a cleavage reaction feed to a cleavage  
        reactor to produce a cleavage reaction mixture  
        comprising the one or more hydroperoxides; and  
    subjecting the cleavage reaction mixture to cleavage  
15 reaction conditions effective to produce a  
    cleavage reaction product comprising phenol and  
    one or more component selected from the group  
    consisting of methyl ethyl ketone (MEK),  
    acetone, and combinations thereof;  
20 wherein the cleavage reaction conditions comprise a  
    cleavage reaction temperature which is  
    sufficiently high to cleave a majority of the  
    one or more hydroperoxides but sufficiently low  
    to produce a first quantity of non-recoverable  
25 byproducts from components selected from the  
    group consisting of dimethylbenzyl alcohol  
    (DMBA), ethyl methyl benzyl carbinol (EMBA),  
    and combinations thereof, the first quantity of  
    said non-recoverable by-products being less  
30 than a second quantity of said non-recoverable  
    byproducts produced from said components by the  
    same process at a cleavage reaction temperature  
    of 75 °C or higher.

**Brief Description of the Drawings**

35 [0008] Fig. 1 is a schematic diagram of a preferred  
embodiment of the cleavage process.

### Detailed Description

[0009] The "low temperature cleavage" of the present application is run at cleavage temperatures which decrease the loss of DMBA and EMBA to non-recoverable by-products.

[0010] Low temperature cleavage will be described with reference to a preferred embodiment in which the cleavage zone comprises a first cleavage reactor and a second cleavage reactor. However, low temperature cleavage encompasses the use of one or more reactors, and is not limited to a system using two reactors.

[0011] The cleavage reaction feed comprises from about 0.5 wt.% to about 2 wt.% water, a ketone stream selected from the group consisting of an acetone stream, a MEK stream, or a mixed acetone/MEK stream, and hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof. It has been found that a ketone feed, preferably from the ketone recovery zone(s) is an aid in reducing production of non-recoverable by-products from DMBA and/or EMBA. When the cleavage reaction occurs in a single reactor, the cleavage reaction mixture is first exposed to first reaction conditions (described below) comprising a relatively low temperature, and subsequently exposed to second reaction conditions (also described below) in the same reactor. In a preferred embodiment, the initial cleavage reaction feed is a first cleavage reactor feed 26 (Fig. 1) to a first cleavage reactor 12.

[0012] The cleavage reactor(s) may be a variety of reactor types. Preferred reactors include, but are not necessarily limited to plug-flow reactors ("PFR's"); plug-flow reactors with recycle (PFRR's); and continuous stirred tank reactors (CSTR's).

[0013] The first cleavage reactor 12 can be a stirred tank reactor with associated internal or external heat exchange equipment effective to maintain the first cleavage reaction mixture at the first cleavage reaction temperature. In a preferred embodiment the first

cleavage reactor 12 is a pipeline loop reactor comprising one or more heat exchangers 14, 16 at appropriate locations to provide cooling sufficient to maintain the first cleavage reaction mixture at the first cleavage reaction temperature. Generally, the first cleavage reaction temperature is from about 45°C to about 70°C. In a preferred embodiment, the first cleavage reaction temperature is from about 45°C to about 60°C, more preferably from about 45°C to about 55°C. The first cleavage reaction pressure is maintained sufficiently high to maintain the first cleavage reaction mixture in the liquid phase. Operating at 0.5 atmosphere or more generally is sufficient to maintain the first cleavage reaction mixture in the liquid phase.

[0014] A pump 18 is installed in the pipeline loop to provide for recirculation of a recycle flow of the first cleavage reaction mixture through the first cleavage reactor 12. A second portion of the first cleavage reaction mixture, the "first cleavage reaction product," is withdrawn from the pipeline loop reactor at a withdrawal point 20 located a short distance upstream of the feed point 22 for the first cleavage reactor feed 26. The recycle flow 24 through the pipeline loop of the first cleavage reactor 12 is much larger than the flow of the first cleavage reactor feed 26 (sometimes referred to as the "first cleavage reactor feed flow 26"). Preferably, the ratio of the recycle flow 24 to the first cleavage reactor feed flow 26 is from about 10:1 to about 100:1 on a weight basis, and more preferably from about 20:1 to 40:1 on a weight basis.

[0015] The first cleavage reaction conditions comprise a first cleavage reaction residence time effective to cleave from about 95% to about 98% of hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof. Depending upon the hydroperoxides present in the first cleavage reaction mixture, the hydroperoxides are converted to phenol and a compound selected from the

group consisting of methyl ethyl ketone (MEK), acetone, and combinations thereof. Generally, the first cleavage reaction residence time is from about 1 minute to about 10 minutes.

5 [0016] The first cleavage reaction conditions comprise an acid catalyst effective to catalyze the cleavage of s-butylbenzene hydroperoxide and (if present) cumene hydroperoxide. Suitable acid catalysts include but are not necessarily limited to sulfuric acid, sulfuric acid  
10 anhydride, perchloric acid, and phosphoric acid. A preferred acid catalyst is sulfuric acid. In a preferred embodiment, the acid catalyst 28 (preferably concentrated sulfuric acid), is added to a reaction mixture side stream 27 at one or more acid addition points 29. The  
15 reaction mixture side stream is located between the first cleavage reaction product withdrawal point 20 and the first cleavage reactor feed point 22.

[0017] The acid catalyst is used in an amount of from about 0.005% to about 0.1% by weight based on the first  
20 cleavage reactor feed flow 26. Concentrated sulfuric acid and other suitable acid catalysts are commercially available from a variety of sources.

[0018] The first cleavage reaction product 32 is fed to a second cleavage reactor 30, preferably a once through plug  
25 flow reactor, to produce a second cleavage reaction mixture. The second cleavage reactor 30 is operated at second cleavage reaction conditions effective to produce a second cleavage reaction product 44 (SCRP). The first  
30 cleavage reaction product preferably is heated to a second cleavage reaction temperature and maintained in the second cleavage reactor 30 for a second cleavage reaction residence time effective to perform one or more,  
preferably all of the following functions: cleave greater than 95 wt.% of remaining hydroperoxides present in the  
35 first cleavage reaction product; convert 60 wt.% or more, preferably 75 wt.% or more, preferably 85 wt.% or more of DMBA (if present) in the first cleavage reaction product to AMS; and, convert 60 wt.% or more, preferably 75 wt.%

or more, preferably 85 wt.% or more of EMBA (if present) in the first cleavage reaction product to AES and 2P2B.

In this preferred embodiment, selectivity of conversion of DMBA to AMS and/or of EMBA to AES and 2P2B is maximized.

5 Generally the second cleavage reaction residence time is from about 5 seconds to about 1 minute.

[0019] Suitably, the second cleavage reaction conditions comprise a second cleavage reaction temperature of from about 60 °C to about 130 °C, preferably from about 70 °C to

10 about 120 °C. The second cleavage reaction conditions also comprise a second cleavage reaction pressure which, when combined with the second cleavage reaction temperature, is sufficient to maintain the second cleavage reaction mixture in the liquid phase. At the foregoing

15 temperatures, a pressure of about 30 psig or more is sufficient. The second cleavage reaction product 44 is withdrawn from the second cleavage reactor 30 and passed to additional stages for recovering the cleavage products.

[0020] By increasing the yield of AMS, AES, and 2P2B, the 20 low temperature initial cleavage effectively reduces the amount of cumene and s-butylbenzene required to co-produce a given amount of phenol and MEK and/or acetone. Conversion efficiency is improved and the formation of non-recoverable by-products during cleavage is reduced.

25 [0021] Depending on the ratio of s-butylbenzene hydroperoxide to cumene hydroperoxide, the cleavage produces a second cleavage reaction product 44 with molar acetone:phenol ratios from about 0.8:1 to about 0.23:1. Molar MEK:phenol ratios in the second cleavage reaction 30 product 44 are from about 0.2:1 to about 0.77:1. In a most preferred embodiment, the acetone to phenol ratio in the second cleavage reaction product 44 varies from about 0.44:1 to about 0.25:1.

[0022] Reactions which occur at lower temperatures occur 35 in the early cleavage stages, preferably in the first cleavage reaction, which occurs in the first cleavage reactor 12. About 95% to about 98% conversion of hydroperoxides to phenol and MEK and/or acetone is

achieved in the first cleavage reactor 12. Reactions which require higher temperatures occur in the later cleavage stages, preferably in the second cleavage reactor 30. The conversion of DMBA to AMS and EMBA to AES and 2P2B require relatively high temperatures of from about 70 °C to about 130 °C and these reactions are postponed, preferably until the first cleavage reaction product 32 reaches the second cleavage reactor 30. At this point, little hydroperoxide remains to be cleaved. The second cleavage reaction conditions can be optimized to maximize the conversion of DMBA to AMS and EMBA to AES and 2P2B.

[0023] In a preferred embodiment, the safety of the cleavage reaction is enhanced compared to other embodiments. By using a pipeline loop reactor as the first cleavage reactor 12, it is possible to make multiple exotherm measurements to verify that the reaction is being carried properly and to control the amount of acid catalyst added to the first cleavage reaction mixture side stream 27. In typical boiling pot cleavage reactors, acid addition typically is controlled by the single exotherm measurement taken at the sulfuric acid addition point. The single exotherm measurement is made by pumping a small amount of the cleavage reactor mixture out of the reactor at the acid addition point and mixing that small amount of the cleavage reaction mixture with acid. The exotherm generated upon acid addition is measured for process control and to determine if a shutdown is required for safety purposes. If the reaction is running well, then the exotherm measured is moderate (typically 15 °C). If the reaction is running too fast, then no exotherm is measured. If the exotherm is large (about 25 °C or more), then the reaction is running too slowly. The risk of the reaction running too slowly is that a runaway reaction can occur when additional acid is added.

[0024] Plug flow reactors (PFR's) and plug flow reactors with recycle (PFRR's) are especially adaptable to multiple exotherm measurements. Controlling acid addition based on

multiple exotherm measurements lowers the risk of adding too little or too much acid catalyst to the first cleavage reactor 12 due to an incorrect exotherm measurement by any one failed control system component, and essentially  
5 decouples safety components from control components.

[0025] In a preferred embodiment, the exotherm preferably is measured at multiple locations. The exotherm is measured across one or more reaction mixture exotherm measurement points, preferably a first reaction mixture  
10 side stream exotherm measurement point 51 (or a first RMSEM point 51) and a second RMSEM point 50 along the reaction mixture side stream 27. The exotherm also preferably is measured in the first cleavage reactor 12 across one or more first cleavage reactor (FCR) exotherm  
15 measurement points, preferably a first FCR exotherm measurement point 30 and a second FCR exotherm measurement point 31 along the first cleavage reactor 12. The exotherm also preferably is measured across the second cleavage reactor, preferably across a second cleavage  
20 reactor (SCR) entry exotherm measurement point 40 and a second SCR exit measurement point 41.

[0026] The second cleavage reaction product 44 generally is fed to a neutralization apparatus and may be treated using known procedures for producing phenol and other  
25 products, depending upon the oxidation feed.

[0027] Persons of ordinary skill in the art will recognize that many modifications may be made to the foregoing without departing from the spirit and scope thereof. The embodiment described herein is meant to be illustrative  
30 only and should not be taken as limiting the invention, which will be defined in the claims.